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(54) Title: ETCHING SOLUTION AND METHOD

(57) Abstract: An etching solution of Hydrogen Fluoride (HF), carboxylic acid and water having a high etch selectivity for silicon oxide relative to metal, polysilicon and nitride. The etching solution is created by injecting anhydrous HF into a carboxylic acid having a precisely controlled minimal amount of water. The etching solution is useful in the fabrication of Micro Electro-Mechanical System (MEMS) devices, as well as the fabrication of MEMS devices in combination with integrated electronics on the same chip.

ETCHING SOLUTION AND METHOD

Field of the Invention

The present invention relates, in general, to an etching solution and, more particularly, to an etching solution for etching semiconductor and Micro Electro-Mechanical System (MEMS) devices.

Background of the Invention

The deposition and etching of dielectric and metal layers to form MENS devices such as micro-sensors, micro-actuators and micro-switches is generally known as micro-machining. Etching of a sacrificial dielectric layer, such as silicon dioxide, is an important micro-machining method employed in the fabrication of MEMS devices as well as in the formation of semiconductor devices.

The sacrificial oxide is typically provided in a polysilicon structure that may also include silicon nitride and metallization, e.g. aluminum or copper. When etching the sacrificial oxide, it is desirable to minimize the extent to which the polysilicon, metal and nitride materials that form portions of the final structure are etched by the sacrificial oxide etching solution.

The extent to which a particular etching solution etches non-oxide materials is characterized by the etch selectivity of the solution. For MENS and other semiconductor devices, a high etch selectivity for oxide relative to metal, for example, is desirable. One prior etching solution is a so-called Buffered Oxide Etch (BOE) solution that contains HF buffered by arnmonium fluoride. However, the BOE solution exhibits poor etch selectivity in that this solution severely etches exposed metal, polysilicon, and/or nitride surfaces during the etching of the sacrificial oxide. In particular, aluminum

metallization is often completely etched before the sacrificial oxide is removed in its entirety.

A common use for micro-machining as described above is the formation of a MEMS sensor. Furthermore, it is becoming desirable to form integrated electronics on the same device used to form the MEMS sensor. Thus, when forming a combination MEMS sensor, which requires the etching of a sacrificial oxide, and an integrated circuit, it is critical that the metallization and passivation features of the chip not be detrimentally etched by the sacrificial oxide etching solution.

Accordingly, it is desirable to provide a chemical solution for etching a sacrificial oxide having a high etch selectivity for silicon oxide relative to metal, polysilicon, and nitride and which is suitable for the fabrication of MENS devices and electronic devices on the same chip.

Detailed Description

The present invention generally provides an etching solution that is a mixture of anhydrous HF, a carboxylic acid and water. The solution is useful for the etching of oxides used in the fabrication of MEMS devices such as, for example, micro-sensors and micro-machines. An important advantage of the etching solution of the present invention is that it has a high etch selectivity for silicon oxide relative to other materials including metals, nitrides and polysilicon that form the structural components of MEMS and electronic devices. As a result of this etch selectivity, the etching solution of the present invention can remove sacrificial oxides with only relatively minor etching of these other non-oxide materials. Thus, the etching solution of the present invention improves the fabrication process of MEMS and electronic devices.

The etching solution is described further below in one

embodiment of the present invention with an example of its use PhosphoSilicate Glass (PSG) created by chemical vapor deposition. Thermally grown SiO_2 and PSG are two examples of oxide films used as a sacrificial oxide layer in the formation of a micro-machined structure. Typically, the sacrificial oxide layer is in contact with portions of the micro-structure prior to sacrificial oxide etching. However, one of ordinary skill in the art will recognize that the etching solution is also generally applicable to the removal of other types of oxides that may be used in MEMS and electronic devices where metals, nitrides and/or polysilicon materials that form the micro-structure or electronic components could be exposed to the etching solution during oxide removal.

The high etch selectivity of the present etching solution permits the removal of the sacrificial oxide without significant degradation of the exposed metal, nitride or polysilicon surfaces. One important result is that electronic devices, e.g., Complementary Metal Oxide Semiconductor (CMOS) devices, can be integrated in a practical process flow onto the same chip used to form the MEMS device.

Prior art etching solutions used to remove the sacrificial oxide layer, such as buffered HF, had the deleterious effect of etching the exposed metal surfaces such as aluminum and copper. However, the use of a carboxylic acid combined with a controlled amount of water, as a solvent or dilutent for HF has been found to overcome the problem of undesirable metal etching. It is believed that the carboxylic acid, combined with a controlled amount of water, in the etching solution slows the dissolution rate of aluminum. Experimental results have confirmed that an etching solution of anhydrous HF, a carboxylic acid, and a controlled amount of water exhibits significantly reduced etching of metals such as aluminum and copper, as well as exhibiting a relatively minimal etch rate of polysilicon and silicon nitride.

The carboxylic acid used can be selected generally as any acid having one or more carboxyl groups and more specifically

including, for example, oxalic acid, formic acid, lactic acid, tartaric acid, malic acid, succinic acid, citric acid and acetic acid. It has been found that acetic acid, combined with the above identified ingredients, is particularly useful for selectively etching thermally grown SiO_2 and PSG.

The mixing ratio of anhydrous HF to carboxylic acid is not considered to be critical, but it has been found that a preferred range is approximately 0.1% anhydrous HF, up to the solubility limit of the particular carboxylic acid. One preferred mixture, which has shown superior experimental results is approximately 10% anhydrous HF relative to the carboxylic acid. Dilution of the solution with respect to the amount of HF, will result in slower etch rates. It should be understood that the mixing ratio of anhydrous HF to carboxylic acid is not a limitation of the present invention.

More important is the need to control the amount of water in the etching solution. The preferred range of water introduced to one embodiment of the present etching solution is in the range of approximately 0.5% to 5.0% by weight. Furthermore, use of an anhydrous carboxylic acid, e.g., glacial acetic acid, is preferred in order to more precisely control the amount of water in the etching solution.

The etching solution is created by injecting anhydrous HF into an aqueous solution of a carboxylic acid, such as glacial acetic acid, having a precisely controlled minimal amount of water. The proportions of the chemicals used for mixing are as described above.

The temperature required for use of the etching solution according to the present invention is not considered to be critical. In general, during etching it is preferred to use a cooler temperature of below approximately 30 degrees Celsius (°C), e.g., in the range of approximately 15°C-30°C. An advantage of such a cooler temperature is a reduction in the evaporative loss of the etching solution. Also, it is preferable that the etching solution is in the

liquid phase during etching.

Furthermore, it is preferred that the etching solution and device having a sacrificial oxide to be etched be placed in a sealed environment substantially free of non-solution water. For example, a sealed container or etching bath with a closed lid having been purged with an inert gas such as nitrogen can be used. It has been discovered that water absorption from the atmosphere above the controlled minimal water levels of the etching solution undesirably increases the metal etching rate.

A working example of the use of anhydrous HF, glacial acetic acid, and water is provided below, only for the purpose of further illustration and is not intended to limit the scope of applicability of the present invention. As discussed hereinbefore, the preferred embodiment of the present invention is applicable to and useful for a wide variety of oxide sacrificial layers, micro-structures, and electronic components.

Example

A mixture of anhydrous HF (10%), glacial acetic acid (89%) and water (1%), by weight, was prepared and used to etch a sample device having aluminum silicon alloy, doped polysilicon, silicon nitride, thermally grown SiO_2, and PSG surfaces. The etching was performed at 18 °C. and the sample etch rates measured as follows:

Material	Etch Rate (angstroms/minute)
Al:Si	2-15
Polysilicon (doped)	0.5-2.0
Silicon nitride	4-14
Thermally grown SiO_2	130-160
PSG	10,000–100,000

Etch selectivities of sacrificial oxides relative to metals, polysilicons, and nitrides are derived from the associated

etch rates. When using an etching solution of HF, carboxylic acid, and a minimal controlled amount of water, approximately in the ratio of 10:89:1, the etch selectivity for thermally grown SiO_2 relative to aluminum or copper is in the range of approximately 9 to 80; whereas, the etch selectivity for thermally grown SiO_2 relative to polysilicon is in the range of approximately 65 to 320. The etch selectivity for thermally grown SiO_2 relative to silicon nitride is in the range of approximately 9-40.

When using the same etching solution for a PSG sacrificial layer, the etch selectivity for PSG relative to aluminum or copper is in the range of approximately 666 to 50,000. The etch selectivity for PSG relative to polysilicon is in the range of approximately 5,000 to 200,000. The etch selectivity for PSG relative to silicon nitride is in the range of approximately 714 to 25,000. The wide range of etch selectivities for PSG is dependent on certain process parameters which include, but are not limited to whether the PSG film is annealed, the phosphorous doping level and the deposition temperature.

It has been discovered that controlling the amount of water in the etching solution to relatively small levels by the use of anhydrous HF and carboxylic acid, results in even more dramatic improvement in etch selectivity, especially with respect to aluminum and copper. The etch selectivity generally increases as the free water content of the etching solution decreases. The etch selectivities with respect to polysilicon and nitride are also high in the controlled minimal water embodiment.

By now it should be appreciated that there has been provided a novel etching solution of anhydrous HF, carboxylic acid, and water that is useful for etching sacrificial oxides during fabrication of MEMS devices. The etch selectivity of the present etching solution for sacrificial oxide layers relative to polysilicon, nitride, and metal is significantly higher than for prior sacrificial oxide etching

solutions and now permits the practical integration of MEMS devices on the same chip as integrated circuit electronics.

Although the invention has been particularly shown and described with reference to an exemplary and preferred embodiment, it will be understood by those skilled in the art that changes in form and detail may be made therein without departing from the spirit and scope of the invention. For example, other suitable metals besides copper and aluminum can include alloys of aluminum and alloys of copper.

Claims

1. An etching solution, comprising:
anhydrous hydrogen fluoride;
a carboxylic acid; and
water.

2. The etching solution of claim 1, wherein the carboxylic acid comprises at least one member selected from the group consisting of oxalic acid, lactic acid, tartaric acid, malic acid, succinic acid, citric acid and acetic acid.

3. The etching solution of claim 1, wherein the etching solution is characterized by an etching rate of a metal in the range of approximately 2 to 15 angstroms/minute, wherein the metal is selected from the group of metals consisting of aluminum, an alloy of aluminum, copper, and an alloy of copper.

4. The etching solution of claim 1, wherein the etching solution is made by injecting the hydrogen fluoride in a gaseous phase into a solution of the carboxylic acid and the water in a ratio of approximately 10:89:1 parts by weight hydrogen fluoride to carboxylic acid to water.

5. The etching solution of claim 1, wherein the etching solution is comprised of an amount of the water in the range of approximately 0.5% to 5% by weight.

6. A method for manufacturing a component having a dielectric material, comprising:

providing an etch solution comprising:

an aqueous mixture of water and a carboxylic acid; and

hydrogen fluoride; and

using the etch solution to etch the dielectric material.

7. The method of claim 6, wherein providing the etch solution comprises:

forming an aqueous mixture of water and a carboxylic acid; and

injecting an anhydrous hydrogen fluoride into the aqueous mixture of water and the carboxylic acid.

8. A method of producing an etching solution, comprising:

forming an aqueous mixture of water and a carboxylic acid; and

injecting an anhydrous hydrogen fluoride into the aqueous mixture of the water and the carboxylic acid, such that an amount of water in the etching solution is in the range of approximately 0.5% by weight to approximately 5% by weight.

9. A method for manufacturing a semiconductor component, comprising:

providing a substrate having a dielectric material disposed thereon; and

etching a portion of the dielectric material using an etching solution comprising:

hydrogen fluoride;

a carboxylic acid; and

water.

10. A method for manufacturing a Micro Electro-Mechanical System (MEMS) component, comprising:

providing a substrate having a dielectric material disposed thereon; and

etching a portion of the dielectric material using an etching solution comprising:

hydrogen fluoride;

a carboxylic acid; and

water.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/311 C09K13/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 824 601 A (DAVISON MICHAEL J ET AL) 20 October 1998 (1998-10-20) the whole document	1-10
X	US 4 395 304 A (KERN WERNER ET AL) 26 July 1983 (1983-07-26) the whole document	1-3,5,6, 9,10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5824601	A	20-10-1998	NONE	
US 4395304	A	26-07-1983	NONE	